

Micron-scale mapping of sulfur cycling across the oxycline of a cyanobacterial mat

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We present a parallel microgeochemical and microbiological study of μm -scale sulfur cycling within hypersaline microbial mats from Guerrero Negro, Baja California Sur, Mexico. Diel variations (day/night) in sulfur cycling were investigated in field incubations as well as in mats grown under controlled conditions in the laboratory at NASA Ames Research Center. Sulfur cycling in the laboratory mats was examined under a variety of different sulfate concentrations to evaluate the role this had on sulfide concentration and isotopic composition. Sulfate levels in the overlying water column were: 80 mM SO_4 (natural level at Guerrero Negro); 1 mM SO_4 ; and 200 μM SO_4 . Dissolved sulfide within the mat was captured on silver discs and analyzed for its abundance and $\delta^{34}\text{S}$ isotopic composition using high resolution secondary ion mass spectrometry (SIMS) on a Cameca 7F Geo.

Two-dimensional microgeochemical mapping reveals well-defined variations in sulfide concentration and $\delta^{34}\text{S}$ with depth down to 1cm below the mat surfaces. Significant sulfide accumulation began ~ 2.5 mm below the surface in daytime incubations and at the mat surface during night incubations. Sulfide concentrations increased with depth until ~ 2.5 and 5 mm below the mat surface for night and day incubations, respectively. Sulfide $\delta^{34}\text{S}$ decreased with depth by ~ 20 permil over the first ~ 2 mm of sulfide deposition in both day and night incubations. At deeper levels, sulfide $\delta^{34}\text{S}$ continued to vary gradually (up to 5 permil/mm). These variations in sulfide abundance and isotopic composition are attributed to spatially variable bacterial sulfate reduction within the mat. A parallel CARD-FISH study of known sulfate-reducing bacteria shows they are organized in several distinct layers, as well as dispersed throughout the mats. The spatial distribution of these microorganisms is consistent with the variation in sulfide concentration and isotopic composition we have observed in each of our incubations.

Ln(III) coprecipitation with trioctahedral smectite hectorite

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Clay minerals may play an important role in a high-level nuclear waste (HLW) repository system. They may form as secondary phases upon alteration of the waste matrix over geological timescales. The formation of these phases represents a significant retention potential for radionuclides including the actinides, which dominate the long-term radiotoxicity of HLW [1]. The actinides Am and Cm always occur as trivalent ions, and under the reducing conditions of a HLW repository, some fractions of Pu(III) may also occur.

Radionuclide immobilization by incorporation into the bulk structure may occur via coprecipitation. In recent lab-scale experiments, Cm(III) and Eu(III) (as a chemical non-radioactive homologue) were coprecipitated with hectorite, a smectite forming under HLW near-filed conditions [2]. Time-resolved laser fluorescence spectroscopy (TRLFS) data suggested that an octahedral substitution mechanism may operate [3] and powder EXAFS spectra suggested that Eu is 6-fold coordinated by O, as in a Mg structural site [4].

Based on this background, we synthesized hectorite in the presence of Eu(III) or Lu(III). The multi-step formation of organo-hectorite [5] allowed to track Eu(III) by low-temperature site-selective TRLFS. Data indicated that Eu is located at an octahedral site in the precursor and in the organo-clay. Polarized-EXAFS experiments were carried out for self-supporting films of Eu(III) or Lu(III)-containing organo-clay: data showed that Lu is surrounded by O at 2.26 Å, a distance typical of 6- to 7-fold coordination. Higher Mg (3.12 Å) and Si (3.26 Å) neighboring shells were detected, suggesting that Lu is located in a clay-like environment.

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